EFFECT OF REDUCED SALINITY INPUT ON RIVER STRATIFICATION AND DISSOLVED OXYGEN

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Abstract. Changes in the occurrence, character, and longitudinal extent of salinity (S) stratification, and related impacts on dissolved oxygen (DO), in the Seneca and Oswego Rivers, NY, in response to the abatement of ionic pollution of inflowing Onondaga Lake, is documented. The analysis is based on vertical profiles of specific conductance and DO collected over a 20 km reach of the river system for several years before and after the closure of the source of the ionic pollution, a soda ash manufacturing facility. The S difference between the lake and the Seneca River decreased from about 2.6 to 0.7 parts per thousand (‰) following the closure; more than 50% of the continuing difference is associated with lingering ionic waste loading from soda ash production. The occurrence and longitudinal range of the S stratification phenomenon was, and continues to be, highly dependent on river flow. It is most strongly manifested when river flow is low. The occurrence, magnitude, and longtitudinal extent of S stratification have decreased, and vertical exchange between the stratified layers has increased, since the closure, thereby ameliorating the coupled negative impact on the river's oxygen resources. However, under low flow conditions (e.g., probability of occurrence equal to 15%) S stratification continues to e::tent > 2 km upstream and > 8 km downstream of the point of entry of Onondaga Lake into the Seneca River. Severe DO depletion in the lowel river layer, representing violations of New York water quality standards, continues to occur where S stratification prevails. Elimination of the continuing ionic waste inputs from soda ash production would further limit the stratification phenomenon and improve the river's DO problem.

Key words: salinity, stratification, oxygen depletion, ionic waste, river

1. Introduction

Density stratification is attributable solely to thermal stratification in the vast majority of fresh water systems, because the influences of salinity (S) and depth (pressure) are usually insignificant (Chen and Millero, 1977). The phenomenon is observed rarely in inland rivers, and usually only briefly in relatively deep systems where turbulence is low. Salinity-based density stratification is observed in coastal rivers proximate to their entry into estuaries. The presence of a vertical density gradient limits exchange between the layers, which promotes the development of gradients in nonconservative substances such as oxygen.

Effler *et al.* (1984) reported the occurrence of S-based density stratification in an inland river system that was a result of ionic pollution, and demonstrated it negatively impacted the oxygen resources of the lower layer of the river(s). Here

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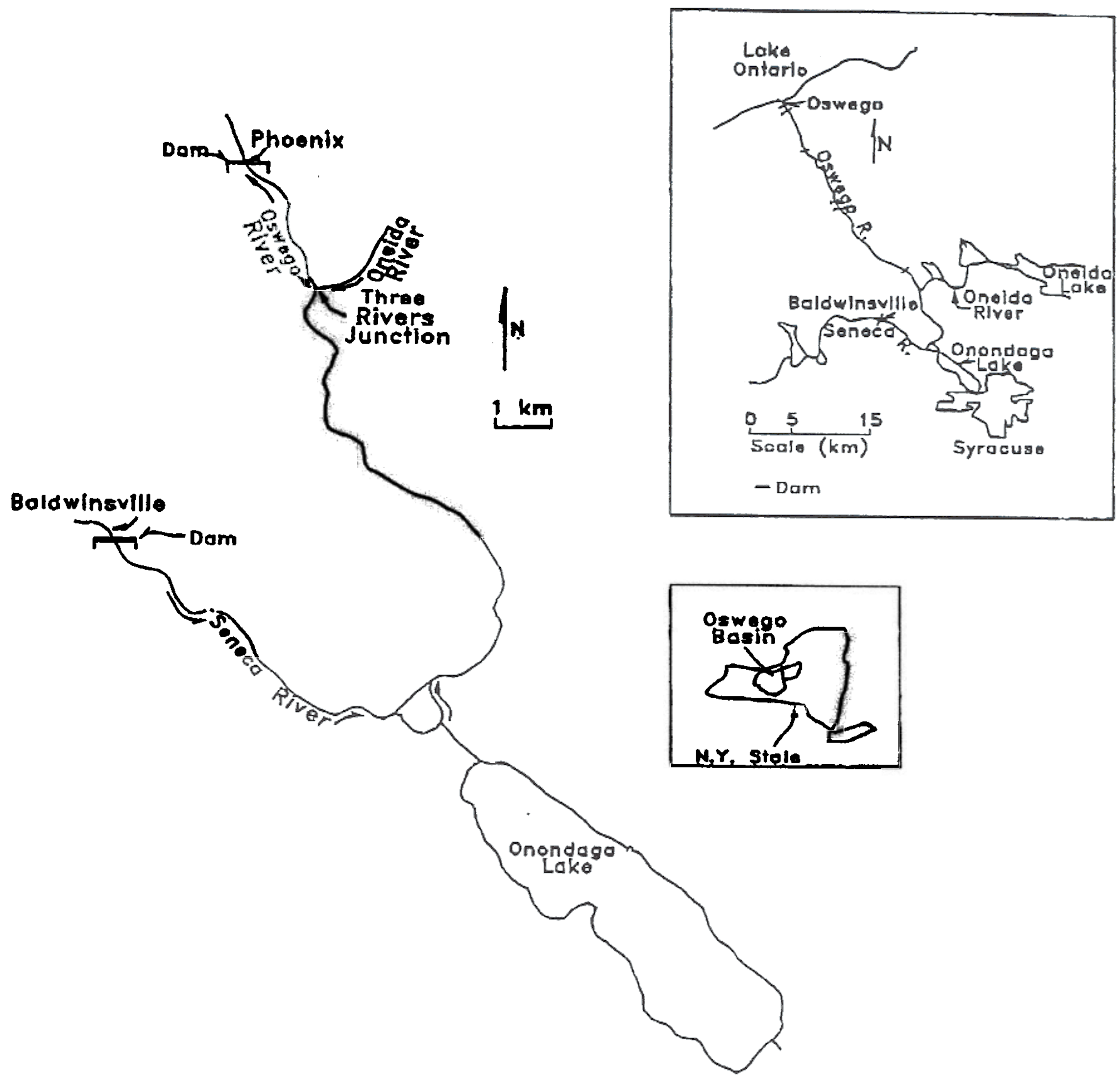

Figure 1. Study portion of Three Rivers system, with insets (2) of the larger river system and the position of the Oswego River basin within the state of New York.

we document changes in the character of *S* stratification and related impacts on dissolved oxygen (DO), for the same system, that have occurred in response to the abatement of the ionic pollution. Lingering impacts are linked to continuing inputs of ionic waste.

2. Description of Study System

2.1. THE SENECA AND OSWEGO RIVERS, AND ONONDAGA LAKE

The Seneca and Oswego Rivers are part of the Three Rivers system (Oswego River basin, Figure 1) which drains about 13,200 km^2 of central New York state to Lake Ontario. A schematic of the portion of the system included in this study is presented in Figure 1. The Seneca River combines with the Oneida River at the Three Rivers junction to form the Oswego River, which flows in a northerly direction, entering Lake Ontario at the City of Oswego, 34 km downstream of Phoenix (Figure 1). The outflow from Onondaga Lake, that carries the ionic pollution, exits the lake via a 1.9 km channel, entering the Seneca River about 12 km upstream of the Three Rivers junction. During summer low flow periods the inflow from the lake can increase the flow of the river by as much as 40% (e.g., Canale *et al.*, 1995), however, on average, the lake inflow only increases the river flow measured at Baldwinsville (Figure 1) by about 17%.

The natural flow and mass transport characteristics of this river system have been greatly altered by the construction of dams and navigation locks, forming a part of the New York State Barge Canal. Hydropower facilities are located at many of the dams. The river system is channelized and its depth is relatively independent of river flow, thus variations in river discharge are manifested largely through changes in velocity. The natural gradient along the outlet from Onondaga Lake to the Seneca River was eliminated by dropping the lake level by about 0.6 m in the early 1800s to that of the Seneca River. The level of Onondaga Lake is now regulated by control devices on the three rivers (Figure 1).

Unusual bidirectional flow conditions have been, and continue to be, observed in the lake outlet, particularly during low runoff periods; e.g., Seneca River water flows toward the lake in the upper layer and denser Onondaga Lake water exits out the bottom of the channel (Effler, 1987; Owens and Effler, 1985; Seger, 1980; Stewart, 1978). Elimination of the natural elevation gradient between the lake and the river made the system susceptible to this phenomenon, however, it has largely been driven by the elevated density of the lake caused by ionic pollution. The mostly S-based (Owens and Effler, 1996) density stratification set up under the unusual flow regime in the lake outlet extends out into the river (Canale *et al.*, 1995; Effler *et al.*, 1984).

2.2. Onondaga Lake: Origins of Ionic Pollution

Soda ash (Na_2CO_3) was manufactured by the Solvay process at a facility on the western shore of the lake from 1884 to 1986. Large quantities of ionic (Cl^-, Na^+, and Ca^{2+}) waste accompanied the production of soda ash. Approximately 0.5 kg of NaCl and 1.0 kg of $CaCl_2$ waste were generated and discharged to the lake for each kg of Na_2CO_3 produced (USEPA, 1974). The summed average annual loading of Cl^-, Na^+, and Ca^{2+} from all sources to the lake over the last 12 y of operation of the soda ash facility was 1.2×10^9 kg (Effler and Whitehead, 1996). By 1989 (3 y after closure of the facility) the summed load was about 0.14×10^9 kg, or about 12% of the pre-closure load.

Table I
Description of monitoring programs for Seneca and Oswego Rivers

Year	No. of days	No. of stations	Source
1978	4	7	Effler *et al.*, 1984
1981	2	15	Effler *et al.*, 1984
1982	9		this work
1982	90	10	Calocerinos and Spina, 1984
1990	16	8	this work
1991	42	8–15	this work*
1993	18	6	this work
1994	18	8	this work

* Also see Naumann (1993).

A substantial fraction of the continuing (post-closure) input of these three ionic constituents to the lake is residual ionic waste from the Solvay process. Most of it enters the lake via a natural tributary that runs through the Solvay waste beds (Effler, 1987) of the facility (Effler and Whitehead, 1996). This is manifested as dramatic increases in each of the three ions downstream of the wastebeds (Effler *et al.*, 1991; Effler and Whitehead, 1996), and the maintenance of the ion ratio signatures of the Solvay process waste in the tributary (Effler and Whitehead, 1996). The estimated continuing contributions of Solvay process waste to the total external loads of Cl^-, Na^+, and Ca^{2+} to the lake are 55, 42, and 30%, respectively (Effler and Whitehead, 1996).

The average S of Onondaga Lake the last 17 y of soda ash production was about 3‰; 85% of S was associated with Cl^-, Na^+, and Ca^{2+} (Effler, 1996). Lake concentrations of these ionic species decreased rapidly following closure of the soda ash facility (Driscoll *et al.*, 1994; Effler, *et al.*, 1990) in response to abrupt decreases in loading and the rapid flushing rate of the lake (Doerr *et al.*, 1994). The average S of the lake had decreased to about 1.2‰ by the early 1990s; about 70% of S is presently associated with Cl^-, Na^+, and Ca^{2+} (Effler, 1996). Even at the lower ionic concentrations that prevail since closure of the soda ash facility, the lake S exceeds that of the Seneca River ($S \approx 0.45$‰) during summer low flow periods by about 0.7‰. Thus the salinity difference between the lake and the Seneca River has been greatly reduced, but not eliminated, by the closure of the industry. Elimination of the lingering ionic waste inputs from soda ash production would reduce the S difference between the lake and the river to about 0.2 – 0.3‰, less than half of the prevailing difference.

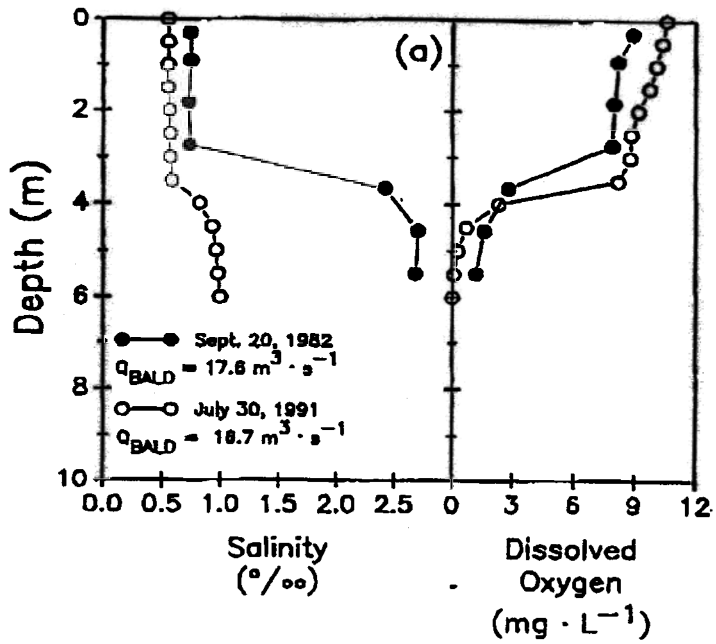

Figure 2. Vertical profiles for the Seneca River: (a) salinity (S), and (b) dissolved oxygen (DO). 1982 case for a location 15 km downstream of Baldwinsville, 1991 case for a location 16 km downstream of Baldwinsville. Q_{BALD} = daily average flow measured at Baldwinsville.

3. Methods

This analysis is based on specific conductance and DO measurements made in the reach of the Seneca and Oswego Rivers between the Baldwinsville and Phoenix dams (Figure 1). Features of the various contributing data sources are described in Table I. Vertical profiles (mostly 1 m depth interval) were collected at various locations, fixed by navigation buoys, and identified here by distance downstream from the Baldwinsville dam (Figure 1). The various programs executed before closure differend greatly with respect to monitoring frequency and the number of sites. Most of the monitoring was conducted over the June-September period.

DO measurements made with field instrumentation (YSI model 54 through 1990, HYDROLAB Surveyor 3 thereafter) were adjusted to match wet DO determinations made at selected sites according to the Winkler titration method (APHA, 1992). Specific conductance at 25 °C was calculated according to the protocol described by USGS (1988) and adopted by HYDROLAB (1991); equivalent internal adjustments were made by the instrumentation used since 1991. Values of S in the river were estimated from specific conductance according to a relationship presented by the USGS (1988) and adopted by HYDROLAB (1991). Flow data used to support this analysis were daily average values reported by USGS for a station located at Baldwinsville (Seneca River; see Figure 1).

4. Results and Discussion

4.1. Occurrence of Stratification: Before and After Closure of Soda Ash Facility

The occurrence of S and DO stratification is illustrated for two days of similar low flow in the Seneca River for a position about 8 km downstream of the Onondaga Lake inflow in Figure 2. The 1982 and 1991 profiles (Figure 2) are representative of conditions before and after closure of the soda ash facility, respectively. The flows on these two days are exceeded about 95% of the time. Two days of similar flow were chosen to normalize for this important mediating influence (see subsequent treatment). Salinity stratification was clearly manifested on both dates (Figure 2a). Two layers of relatively uniform S were separated by a rather abrupt chemocline. The magnitude of S stratification was much greater on the pre-closure date; the S difference between the upper and lower layers was about 1.9‰ for the pre-closure observation and 0.4‰ for the post-closure data. The S values of the upper river layer were similar for the two dates, largely reflecting conditions upstream of the lake. The S values of the lower waters correspond approximately with observations for the upper waters of the lake (Owens and Effler, 1996), clearly depicting the origin of the S stratification as the inflow from ionically polluted Onondaga Lake.

The negative implications of the S stratification phenomenon for the oxygen resources of the lower layer of the river are demonstrated by the paired DO profiles (Figure 2b). DO was severely depleted in the lower layer on both days, approaching anoxia. These conditions represent violations of the minimum DO standard (4.0 mg L^{-1}) for the state of New York. Canale *et al.* (1995) applied a DO model that had been validated for the river system to evaluate processes contributing to the oxygen depletion for the post-closure period. The processes of nitrification, sediment oxygen demand, and phytoplankton respiration were all found to contribute importantly to the DO depletion (Canale *et al.*, 1995). Earlier Effler *et al.* (1984) had attributed the DO depletions largely to respiration and decay of phytoplankton released from Onondaga Lake. Canale *et al.* (1995) found that violations of the DO standard could be avoided by elimination of the S stratification, even for low river flows with a low return frequency of once in ten years. The similarity of the oxygen depletion for the widely disparate magnitudes of S (density) stratification of Figure 2 suggests the level of stratification that persists at lower river flows since closure of the soda ash facility continues to impair vertical mixing sufficiently to severely degrade the river's oxygen resources.

Influence of River Flow

The interplay between the occurrence of S and DO stratification in the river system and the ambient river flow is demonstrated by the paired temporal distributions for selected downstream locations in Figures 3 and 4. The pre-closure example of Figure 3 is for a location 8.9 km downstream of the Onondaga Lake inflow

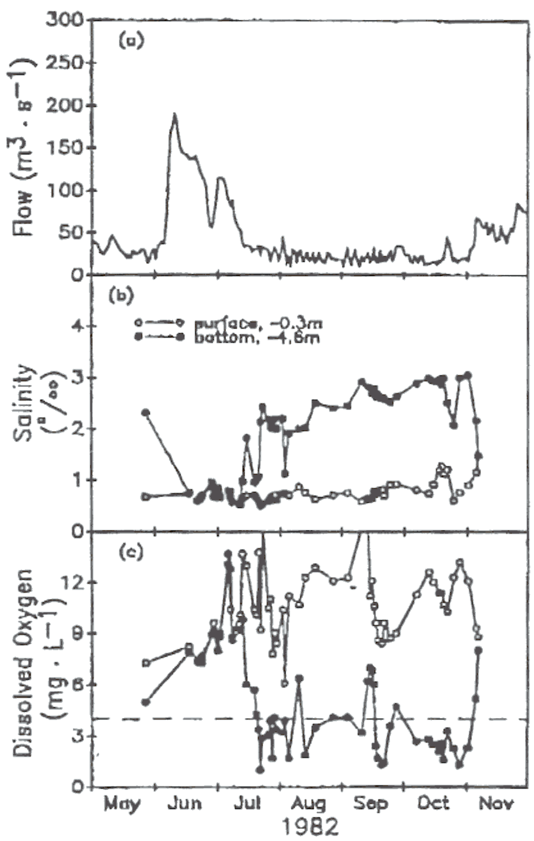

Figure 3. Paired temporal distributions in the Seneca River in 1982: (a) daily average flow, as measured at Baldwinsville, (b) S at surface and near-bottom depths, at a location 17 km downstream of Baldwinsville, and (c) DO at surface and near-bottom depths, at the same location as for S. Dashed line corresponds to the New York water quality standard.

(16.7 km downstream of Baldwinsville). The post-closure example (Figure 4) is for a position 8.2 km downstream of the lake inflow. The variations in flow observed in the two selected years (1982 and 1994) facilitate the resolution of the interplay between flow, density stratification, and DO depletion in the lower river layer.

Clearly river flow was (Figure 3), and continues to be (Figure 4), a strong regulator of the occurrence of the *S* stratification phenomenon. Salinity stratification was well established in late May 1982 (Figure 3b) when the Seneca River flow at Baldwinsville was < 40 m^3 s^{-1} (Figure 3a). The increased vertical mixing associated with the increased flows in June and early July of 1982 eliminated the stratification. However, *S* stratification was re-established with the decrease in flow in early July. Salinity stratification prevailed thereafter until the flow increased to > 50 m^3 s^{-1} in early November (Figure 3). The magnitude of *S* and its generally increasing trend in the lower layer during the interval of stratification (Figure 3b) were consistent with epilimnetic measurements from Onondaga Lake (Doerr *et al.*, 1994; Effler, 1995). The occurrence of substantial DO stratification (Figure 3c) corresponded to that observed for *S* stratification (Figure 3b). The DO was < 4 mg

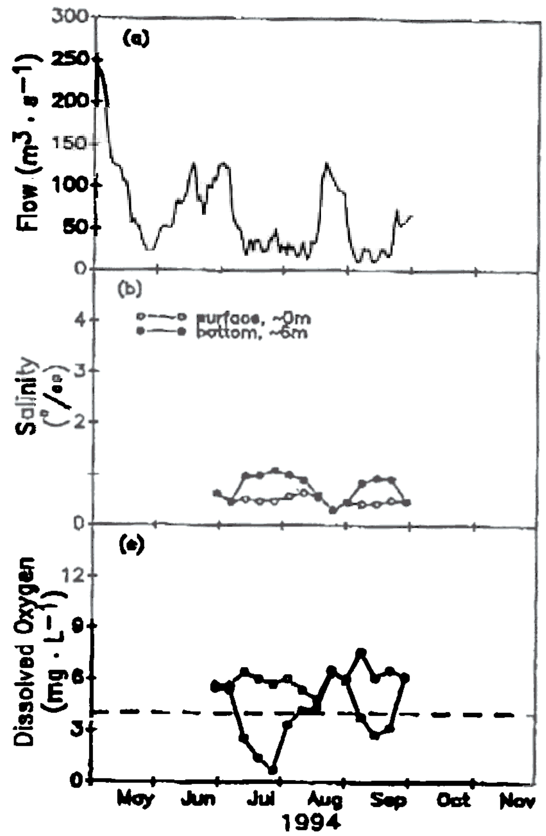

Figure 4. Paired temporal distributions in the Seneca River in 1994: (a) daily average flow, as measured at Baldwinsville, (b) S at surface and near-bottom depths, at a location 15 km downstream of Baldwinsville, and (c) DO at surface and near-bottom depths, at the same location as for S. Dashed line corresponds to the New York water quality standard.

L^{-1} (i.e., violation of New York standard) in the lower layer at this site for most of the late July through October period of 1982. DO concentrations in the lower layer were much more variable than *S*, reflecting the more nonconservative behavior of this constituent and variations in DO demanding substances in the Onondaga Lake outflow (DO, phytoplankton, and ammonia concentrations, and temperature (see Canale *et al.*, 1995)).

The same form of interplay has persisted following the closure of the soda ash facility, though the magnitude of *S* stratification has decreased (Figure 4b), consistent with the decrease in the *S* of the lake (Effler, 1996). The river was unstratified in late June and early July of 1994 when the flow at Baldwinsville exceeded 60 m^3 s^{-1}. *S* stratification prevailed thereafter until mid-August (Figure 4b), when it was broken-up by a runoff event (Figure 4a). Stratification was re-established for most of September when flow < 40 m^3 s^{-1}, and was eliminated again at the increased flow (e.g., > 60 m^3 s^{-1}; Figure 4a) of late September. DO concentrations < 4 mg L^{-1} again prevailed in the lower layer during periods of *S* stratification (Figure 4c). Dramatic year-to-year differences in the timing and duration of *S* stratification and

Table II

Dates and daily average flows in the Seneca River at Baldwinsville for the eight days of Figure 5, with percent exceedance statistics

Data, Cas No.	Flow[a]	% Exceedance[b]
Sept. 20, 1982, Case 1	17.6	95
July 30, 1991, Case 1	16.7	95
July 26, 1982, Case 2	29.7	85
July 18, 1991, Case 2	29.2	85
July 12, 1982, Case 3	53.5	60
May 28, 1991, Case 3	52.4	60
July 8, 1982, Case 4	89.2	40
May 21, 1991, Case 4	75.3	45

[a] Daily average value.
[b] Percent of days for which this is exceeded.

severe DO depletions have occurred and will continue to occur in the river because of natural variations in stream flow (e.g., Figures 3a and 4a) that are common to this region (also see Effler and Whitehead, 1996).

4.3. Changes since Closure of the Ash Facility

Results presented in Figures 2–4 establish that the *S* stratification phenomenon continues to occur in the Seneca River following closure of the soda ash facility. Changes in the character of *S* stratification and coupled impacts on DO are delineated by comparing longitudinal profiles collected at nearly equal river flows from before and after closure of the soda ash facility. Four such comparisons (cases) are presented in Figure 5 (a-d) corresponding to a wide range of flow, from about 17 to 90 $m^3\ s^{-1}$; flows that are exceeded approximately 95 and 40% of the time, respectively. While the selected cases are considered to be generally representative, some variability in conditions both before and after closure has been observed. The dates, corresponding daily average flows measured by USGS at Baldwinsville, and percent exceedance statistics, are listed for the 8 days (4 cases) in Table II.

Note that the 1991 monitoring program depicts *S* stratification extending upstream (> 2 km) at low flows (Figure 5a and b). This 'salt wedge' effect is commonly observed in stratified estuaries (e.g., Thomann and Mueller, 1987) but is unique for inland rivers (Canale *et al.*, 1995). The 'salt wedge' extended > 3 km upstream before closure (Effler *et al.*, 1984), but it was not captured by the spatial resolution of the 1982 measurements incorporated in Figure 5. The *S* of the upper layer increases and that of the lower layer decreases progressively downstream of the lake under stratified conditions (Figure 5) as a result of vertical mixing (Canale *et al.*, 1995; Effler *et al.*, 1984). This longitudinal structure was used as a basis for estimation of vertical mixing coefficients for this portion of the river (Canale *et al.*,

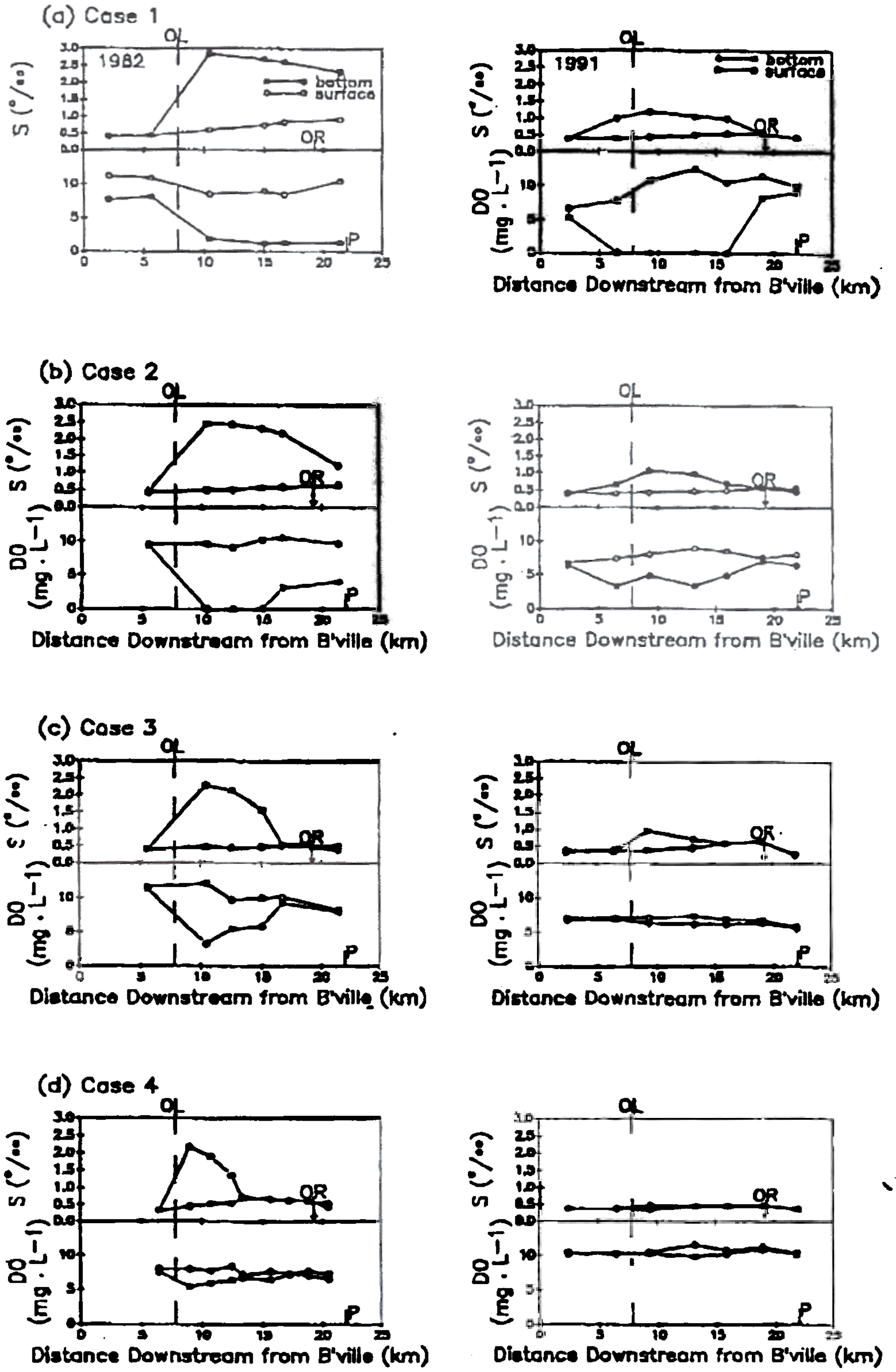

Figure 5. Comparison of paired longitudinal profiles of S and DO for the Seneca and Oswego Rivers for before (1982) and after (1991) closure of the soda ash facility, for four cases of river flow: (a) Case 1, (b) Case 2, (c) Case 3, and (d) Case 4. Cases of increasing river flow (1 to 4), as shown in Table II. Points of entry of Onondaga Lake (OL) and the Oneida River (OR), and the position of the Phoenix dam (P), included for reference.

1995; Effler *et al.*, 1984). In all cases the magnitude of *S* stratification was greater in the river(s) before closure of the soda ash facility (Figure 5), when the lake's *S* was higher.

At the very low flow conditions of Case 1 (Figure 5a; Table II), *S* stratification before closure, and the accompanying severe DO depletion of the lower layer, extended 14 km downstream to the dam at Phoenix (21.8 km downstream of Baldwinsville; Figure 5a; also see Figure 1). Mixing of waters flowing over the dam eliminated *S* stratification downstream of Phoenix (Effler *et al.*, 1984). Following closure, at essentially the same low river flow, *S* stratification, and the attendant DO depletion, was eliminated before the confluence with the Oneida River (Three Rivers junction, Figure 1). Even at the typical summer flow conditions of Case 2 (Table II, flow exceeded about 85% of the time), *S* stratification and coupled DO depletion extended to the dam at Phoenix before closure (Figure 5b). Note the most intensive vertical mixing (e.g., abrupt drop in *S*) occurred near the confluence of the Seneca and Oneida Rivers (19 km downstream of Baldwinsville). S stratification tended to break up even farther upstream at the higher flow of Case 2 following closure of the soda ash facility (Figure 5b). The Case 3 flow is exceeded about 60% of the time (Table II). At this higher flow *S* stratification was eliminated upstream of the Three River junction before closure, but it extended only about 5 km downstream of the lake input following closure (Figure 5c). At the highest flow included in the comparison (Case 4, Table II; flow exceeded about 40–45% of the time), *S* stratification before closure persisted 5 km downstream of the lake input, while following closure it was barely detectable 2 km downstream of the inflow. Only at a river flow of about 120 m^3 s^{-1} (exceeded about 30% of the time) was *S* stratification eliminated in the Seneca River before closure of the soda ash facility.

The reductions in the *S* of Onondaga Lake have clearly reduced the occurrence and the longtitudinal extent of *S* stratification in the Seneca and Oswego Rivers, and thereby ameliorated the coupled negative impact on the oxygen resources of the system (Figure 5).

4.4 ESTIMATION OF CHANGES IN VERTICAL MIXING

The magnitude of *S* stratification affects DO concentration in the stratified bottom waters of the river through its effect on vertical mixing (Canale *et al.*, 1995). It is well known that stable stratification tends to reduce vertical mixing (Fischer *et al.*, 1979). Thus, the bottom waters of the river are not well-mixed with overlying surface waters. In order to directly estimate the effect that reductions in the *S* of Onondaga Lake had on vertical mixing in stratfied portions of the seneca River, a simple mechanistic model of *S* was applied to the river downstream of the lake. This model was based on the assumptions of two uniform layers separated by a sharp interface, steady flow conditions, and that changes in *S* downstream of the lake outlet are caused solely by vertical mixing. Mass S conservation equations applied to the two layers are

$$U_1 \frac{dS_1}{dx} = \frac{v_t}{h_1}(S_2 - S_1)$$

$$U_2 \frac{dS_2}{dx} = \frac{v_t}{h_2}(S_2 - S_1)$$

where U is velocity, h is average depth (layer thickness), x is downstream distance, and v_t is a vertical mass transfer coefficient between the two layers; the subscripts 1 and 2 refer to the surface and bottom layers, respectively. According to this model increases in S_1 and decreases in S_2 moving downstream from the lake (increasing x) are due to the S difference $(S_2 - S_1)$ and vertical mass transfer. Equation (1) was evaluated in difference form, using measurements of S_1 and S_2 at adjacent monitoring stations. The layer thicknesses h_1 and h_2 are from channel bathmetry. The velocities U_1 and U_2 are based on bathymetry and measurements of river flow.

Estimates of v_t as a function of flow at Baldwinsville are presented for four successive length intervals downstream of the lake inflow, for before (1982) and after (1991) closure (Figure 6a–d). While some scatter is evident in the results, several trends emerge. First, for the full range of S stratification conditions considered here, v_t increases as river flow increases. This result is expected because turbulent mixing increases as the flow and velocity increase. Secondly, values of v_t tend to be substantially higher (note log scale for v_t in Figure 6) following closure than prior to closure at the same flow rate, as depicted by the linear least squares regression lines for the two data sets. This is consistent with the decrease in the magnitude of density stratification since closure (e.g., Figure 2a). Thirdly, the differences between pre- and post-closure values of v_t generally decrease as the stream flow increases.

4.5 MANAGEMENT PERSPECTIVES

Clearly the ionic waste discharge from the soda ash facility caused S-based density stratification in the Seneca and Oswego Rivers and thereby negatively impacted the oxygen resources of the river system. The amelioration of these impacts following the reductions in ionic waste discharge from this source that accompanied the closure of the facility, documented herein, further establishes the cause and effect relationship and the responsibility of this facility. Further, it is clear that the residual ionic waste loading from this industrial source continues to foster S stratification in the Seneca River and thereby negatively impact its oxygen resources.

Elimination of the lingering ionic waste loading from soda ash production would undoubtedly further ameliorate the oxygen resource problems of the river, by further reducing the S-based density difference between Onondaga Lake and this Seneca River. This would be manifested as reductions in the occurrence and

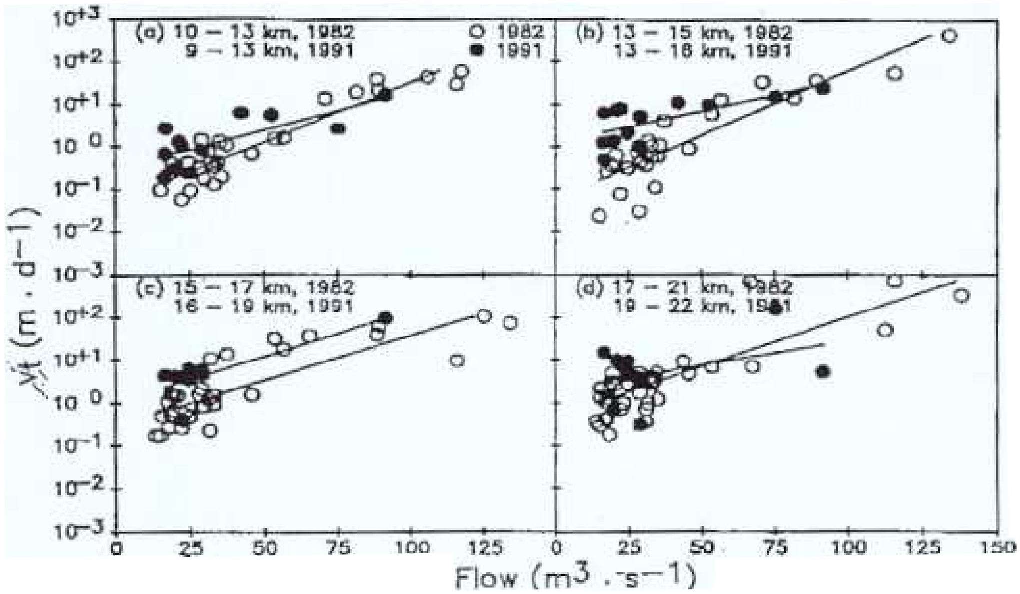

Figure 6. Evaluation of the dependence of v_t, between S stratified river layers, on river flow at several locations (distance from Baldwinsville): (a) 9–13 km, (b) 13–16 km, (c) 15–19 km, and (d) 17–22 km. Best fit linear least squares regression lines included.

longitudinal extent of S stratification in the river. A credible hydrodynamic model of the lake outlet and the Seneca River would be invaluable in establishing the benefit that would be achieved by reducing the S difference between the lake and river. It seems likely that some residual occurrences of density stratification and coupled DO depletion would persist, but would occur more infrequently and over a shorter longitudinal range, associated with natural short-term differences in the temperatures of the river and lake and natural differences in the S (e.g., 0.2–0.3‰) of those systems. This is attributable to the elimination of the natural hydraulic gradient between the lake and river, and should be predicted by the hydrodynamic model. The practicality of eliminating the residual ionic pollution to Onondaga Lake has been questioned (Canale *et al.*, 1995). Alternatively, the continuing density stratification and coupled DO depletion could be remediated by artificially inducing turbulence in the river.

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